

PATENT SPECIFICATION

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(54) CYCLOHEXANE-1,2,3,4,5,6-HEXACARBOXYLIC ACID AND ITS PRODUCTION

5 (71) We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company, of Ludwigshafen/Rhein, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

10 10 The present invention relates to cyclohexane - 1,2,3,4,5,6 - hexacarboxylic acid and to its production.

15 It is known that a form of cyclohexane - 1,2,3,4,5,6 - hexacarboxylic acid can be prepared by hydrogenation of mellitic acid with sodium amalgam (Ann., supplementary volume 7 (1870), page 18, and Ber., volume 28 (1895), page 1272). Mellitic acid is difficultly accessible and the said method is troublesome and unsuitable for industrial use. It is known that several cis-trans isomers of cyclohexane - 1,2,3,4,5,6 - hexacarboxylic acid are possible. The reaction product of the hydrogenation of mellitic acid with sodium amalgam is not a uniform compound. It is a substance which has not been clearly defined and which even after an expensive purification is a hygroscopic viscous syrup which solidifies to form indistinct crystals (cf. the literature references cited above).

20 20 We have now found that a hitherto unknown form of cyclohexane - 1,2,3,4,5,6 - hexacarboxylic acid can be produced by oxidizing bicyclo - (2,2,2) - oct - 7 - en - 2,3,5,6 - tetracarboxylic acid and/or an anhydride thereof with nitric acid of a concentration of from 20 to 100% by weight in the presence of an oxidation catalyst at from 30° to 115°C.

25 25 The cyclohexane - 1,2,3,4,5,6 - hexacarboxylic acid is obtained in good to very good yields by the new process.

30 30 The reaction product is a uniform compound which is clearly defined by elementary analysis, melting point, infrared spectrum and NMR (nuclear magnetic resonance) spectrum.

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It is not identical with the cyclohexane hexacarboxylic acid obtained by hydrogenation of mellitic acid with sodium amalgam and is not contained therein as an isomer as may be shown by reference to the NMR spectra of the isomeric compounds.

35 35 It is known from U.S. Patent Specification No. 3,242,206 and from Ann., volume 611 (1958), page 7, that bicycloheptene and bicyclooctene dicarboxylic acid derivatives can be oxidized to the corresponding tetracarboxylic acids with concentrated nitric acid under forcing conditions. A catalyst is not required for these reactions. It is therefore surprising that when nitric acid is allowed to act on bicyclo - (2,2,2) - oct - 7 - en - 2,3,5,6 - tetracarboxylic acid oxidation to cyclohexane - 1,2,3,4,5,6 - hexacarboxylic acid does not take place. It is only in the presence of an oxidation catalyst that the reaction results in the formation of the hexacarboxylic acid.

40 40 The starting material for the process can be prepared in good yields by the Diels-Alder reaction of maleic anhydride with cyclohexa - 3,5 - diene - 1,2 - dicarboxylic acid (obtainable by partial hydrogenation of phthalic acid). The tetracarboxylic acid, the 2,3 - monoanhydride or the 2,3,5,6 - dianhydride is obtained depending on the reaction conditions and the method of working up.

45 45 Conventional oxidation catalysts, for example compounds of palladium, molybdenum and advantageously of vanadium, may be used for the process of the invention. The oxidation catalysts are preferably used as inorganic salts or oxides. When metal salts are used, the nature of the ion of opposite charge to the ion containing the active metal is not critical. The oxidation state which the active metal assumes in the compounds used is also not critical. Probably the oxidation state necessary for catalysis is set up automatically in the strongly oxidizing reaction medium. Examples of suitable oxidation catalysts are sodium molybdate, sodium vanadate, potassium molybdate, potassium vanadate, ammonium

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5 molybdate, ammonium vanadate, vanadium pentoxide and palladium chloride. The catalyst is advantageously used in amounts of 0.05 to 0.5% by weight with reference to the starting material.

10 Temperatures of from 30° to 115°C, preferably from 50° to 100°C, are used in the reaction. Lower temperatures are not advantageous because of the longer reaction periods which are then necessary. At temperatures higher than 115°C and the conventional reaction periods, in contrast to the prior art methods, the major portion of the starting material is surprisingly recovered unchanged.

15 For example the starting material is recovered to the extent of 80 to 90% after treatment for six hours with 68% by weight nitric acid at 119°C.

20 Nitric acid of a concentration of 20 to 100%, preferably 45 to 100%, by weight is used for the process. It is particularly advantageous to use 50 to 80% by weight nitric acid. If lower concentrations of nitric acid are used, another compound, probably 6,7,8,9-tetracarboxy - 2,4 - dihydroxy - 3 - oxabicyclo - (2,2,3) - nonane - 2,8,4,9 - dilactone, is formed in addition to cyclohexane hexacarboxylic acid to an increasing extent.

25 It is advantageous to use 3 to 7 moles of nitric acid for the oxidation of 1 mole of starting material. It is also possible to use larger amounts of nitric acid but no advantage is gained thereby.

30 Reaction according to the new process in general requires two to twenty-four hours depending on the temperature and the concentration of the nitric acid. The optimum combination of temperature, nitric acid concentration and reaction period may easily be ascertained by preliminary experiment.

35 The reaction may be carried out batchwise or continuously. Batch reaction may be carried out as follows: the starting material is gradually added at the reaction temperature to the nitric acid while stirring, the nitric acid containing the catalyst. The starting material passes into solution and the cyclohexane - 1,2,3,4,5,6 - hexacarboxylic acid formed is precipitated. When the oxidation is over, the reaction mixture is cooled, the reaction product is filtered off and the filtrate either returned or carefully concentrated in vacuo to recover the residual cyclohexane hexacarboxylic acid. The process may be carried

40 out continuously by continuously supplying starting material and highly concentrated, for example 100%, nitric acid to the first vessel of a cascade of vessels so that a definite nitric acid concentration is maintained in the reaction vessels. The cyclohexane hexacarboxylic acid formed is continuously withdrawn from the last reaction vessel of the cascade and filtered off. The filtrate is advan-

tageously recycled to the first reaction vessel of the cascade.

45 Purification of the cyclohexane - 1,2,3,4,5,6 - hexacarboxylic acid is advantageously carried out by converting it into cyclohexane - 1,2,3,4,5,6 - hexacarboxylic trianhydride which is obtained for example by treatment of the reaction product with acetic anhydride. The trianhydride is precipitated whereas byproducts and impurities remain dissolved in the acetic anhydride.

50 The cyclohexane - 1,2,3,4,5,6 - hexacarboxylic acid prepared according to the present process is a valuable intermediate, for example for the production of plastics, lacquers and resins. The esters of cyclohexane - 1,2,3,4,5,6 - hexacarboxylic acid may be used as special plasticizers.

55 The invention is illustrated by the following Examples in which the parts specified are parts by weight.

EXAMPLE 1

60 248 parts of bicyclo - (2,2,2) - oct - 7-en - 2,3,5,6 - tetracarboxylic dianhydride is gradually added with stirring in the course of fifteen minutes to a mixture of 470 parts of 68% by weight nitric acid and 0.5 part of ammonium vanadate which has been heated to 50°C. The temperature of 50°C is maintained during the addition by means of a waterbath. The reaction mixture is stirred for fifteen hours at 55° to 60°C, nitrogen oxides thus escaping. The reaction solution is then cooled to 5°C and the precipitate suction filtered. The filtrate is concentrated in vacuo and a second crop of crystals is isolated. The combined precipitates are washed with acetone and then dried. 325 parts of cyclohexane - 1,2,3,4,5,6 - hexacarboxylic acid (i.e. 93.5% of the theory) is obtained having a melting point of 222° to 224°C (in a closed tube). According to the NMR spectrum it contains three equatorial hydrogen atoms with an absorption at 3.55 ppm and three axial hydrogen atoms with an absorption at 3.10 ppm. The content of byproducts is 1.5%; after purification by way of cyclohexane - 1,2,3,4,5,6 - hexacarboxylic trianhydride (melting point 287° to 290°C) the content of byproducts is less than 0.2%. A cyclohexane - 1,2,3,4,5,6 - hexacarboxylic acid having a melting point of 252° to 255°C is obtained by hydrolysis of the trianhydride.

EXAMPLES 2 TO 4

65 The procedure of Example 1 is adopted but the amounts of catalyst, molar ratios of starting materials to nitric acid, nitric acid concentrations and reaction periods set out in the Table are chosen (lines 2 to 6). The conversion of the starting material, the yield of cyclohexane - 1,2,3,4,5,6 - hexacarboxylic acid and of byproducts are given in lines 7 to 9.

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TABLE

1	Example No.	2	3	4
2	Type and amount of catalyst in % by weight of the starting material	ammonium vanadate 0.2	ammonium molybdate 0.3	ammonium vanadate 0.2
3	Molar ratio of starting material to nitric acid	1:4	1:6	1:5
4	Nitric acid concentration % (wt)	68	68	68
5	Reaction temperature in °C.	80	80	105
6	Reaction period in hours	5	5	2
7	Conversion in %	100	83	100
8	Yield (% of the theory)	91.5	53	63.5
9	Byproducts in %	3.5	21.5	6.5

WHAT WE CLAIM IS:—

1. A process for the production of cyclohexane - 1,2,3,4,5,6 - hexacarboxylic acid which comprises oxidizing bicyclo - (2,2,2) - oct - 7 - en - 2,3,5,6 - tetracarboxylic acid and/or an anhydride thereof with nitric acid of a concentration of 20 to 100% by weight in the presence of an oxidation catalyst at from 30° to 115°C. 10. A process as claimed in any of claims 1 to 9 carried out by gradually adding the starting material to nitric acid containing the catalyst. 40

2. A process as claimed in claim 1 in which the nitric acid used has a concentration of 45 to 100% by weight. 11. A process as claimed in any of claims 1 to 10 wherein the starting material, nitric acid and catalyst are supplied to the first vessel of a cascade of vessels and the reaction product is withdrawn from the last vessel in the cascade. 45

3. A process as claimed in claim 1 or 2 carried out at a temperature of from 50° to 100°C. 12. A process as claimed in claim 11 wherein the reaction product is filtered and the filtrate is returned to the first vessel of the cascade. 50

4. A process as claimed in any of claims 1 to 3 wherein a palladium compound is used as the oxidation catalyst. 13. A process as claimed in claim 1 carried out substantially as described in any of the foregoing Examples. 55

5. A process as claimed in any of claims 1 to 3 wherein a molybdenum compound is used as the oxidation catalyst. 14. Cyclohexane - 1,2,3,4,5,6 - hexacarboxylic acid when obtained by the process claimed in any of claims 1 to 13. 60

6. A process as claimed in any of claims 1 to 3 wherein a vanadium compound is used as the oxidation catalyst. 15. Cyclohexane - 1,2,3,4,5,6 - hexacarboxylic acid, characterised by an NMR spectrum showing an absorption at 3.55 ppm. and an absorption at 3.10 ppm indicating the presence of three axial hydrogen atoms and three equatorial hydrogen atoms, and by a melting point of 222 to 224°C. 60

7. A process as claimed in any of claims 1 to 6 wherein the catalyst is used in an amount of 0.05 to 0.5% by weight with reference to the starting material. 30

8. A process as claimed in any of claims 1 to 7 wherein the nitric acid used has a concentration of 50 to 80%. J. Y. & G. W. JOHNSON,
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9. A process as claimed in any of claims 1 to 8 wherein from 3 to 7 moles of nitric acid is used for the oxidation of each mole of starting material. Chartered Patent Agents,
Agents for the Applicants.